

CRYSTALLINITY VARIATIONS IN THE DOUBLE YIELD REGION

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Abstract. Specimens of a linear low density polyethylene sample were uniaxially deformed up to different elongations to study the double yield phenomenon. Extruded samples were analyzed to calculate the crystallinity, under stressed state and released state (after removal of the stress), using the wide angle X-ray scattering technique. The crystallinity degree associated to the orthorhombic phase of the specimen without deformation was of 55%. This parameter in the stressed state, as a function of the elongation, presented a multi-step behavior. A decrement after the first yield point (48%), then another decrement and an abrupt increment followed by a decrement at higher strain values around the second yield point (28, 40, 30%). The behavior was more notorious in the stressed state than in the released state. The latter results were interpreted in terms of a partial melting followed by a recrystallization process. These experimental findings show that the second yield is not only associated with the deformation of the crystalline region. The partial melting-recrystallization process is one of the main mechanisms of the double yield phenomenon.

Introduction

A yield point in polymers is conventionally accepted as the point where a local maximum is shown in the stress-strain curve (σ - ϵ). At this point a material ceases to deform elastically in a recoverable manner and undergoes permanent plastic deformation¹. Works published for polyethylene²⁻⁷ and other semi-crystalline polymers⁸⁻⁹ have demonstrated the existence of double yield points. The σ - ϵ curve may exhibit comparable values of the stress of the two maxima or a dominant value of either maximum. The stress of the first yield point becomes dominant under extreme conditions of low temperatures, high strain rates or high crystallinities. The second yield becomes dominant under the opposite extreme conditions. The first yield point marks the onset of plastic strains which are slowly recoverable while the second marks the onset of permanent plastic deformation. Different mechanisms exist for each yield process. Two possible mechanisms have been postulated. The plastic deformation is governed by two structurally well-defined processes: a slip of the crystal blocks in the mosaic crystalline structure and a homogeneous shear^{3-4,6}. A qualitative explanation is based on the postulate of a partial melting-recrystallization process during deformation^{2,5}. Most previous work has concerned with the correlation of σ - ϵ behavior and the deformation of the crystalline portion of the material, and little effort has been made to understand the behavior of the crystallinity.

Specimens of a linear low density polyethylene (LLDPE) sample here were uniaxially deformed up to different elongations to calculate the crystallinity, under stressed state (SS) and released state (RS) (after removal of the stress), using the X-ray scattering technique. Since there is a strong correlation between the nature of the yield and the permanent deformation of the material, understanding of the origin of double yielding is very important to understand the mechanisms involved in the complete deformation process.

Experimental

The commercial polymer obtained from Dow Chemical (Dowlex 2101) has a melt index of 1.6 dg/min, and a density of 0.924 g/cm³. Sheets with a uniform average thickness of 1.1 mm were

prepared using a single-screw Brabender extruder, which temperatures at the different zones were set at 150°C and the screw at an angular speed of 70 rpm. Specimens with the standard dumbbell shape with an average width of 7.5 mm were punched out for deformation at 25°C in an Instron tensile testing machine (model 4502). Some experiments were carried out to determine the adequate crosshead speed at which the two yield points are well defined and have comparable stress values. Then, subsequent specimens were stretched with a fixed rate of 10 mm/min up to predetermined elongations in the range where the two yields occur. Every time a new specimen was used. A special x-ray sample-holder, built to maintain the applied stress, was placed in the middle part of the stretched sample; then the sample was cut for X-ray analysis.

Wide angle X-ray scattering (WAXS) patterns were recorded with a Philips horizontal goniometer (PW 1380/60). Cu K α radiation generated at 30 kV and 20 mA was used. The angular position was scanned at 1 °/min and the scattered radiation registered in the interval 5-35°. The x-ray measurements were recorded using stretched samples with the elongation axis held perpendicular to the plane defined by the incident beam and direction of scanning. The elapsed time between the end of the stretching experiment and the beginning of the WAXS experiment was around 10 minutes. The pattern was obtained for the specimen in the stressed state; immediately after this run, the stress was removed (released state) and a second pattern was obtained. Deconvolution using Lorentzian functions was applied to separate the contribution of amorphous and crystalline parts in the angular interval 15.0-27.5°. The crystallinity was calculated in the standard way¹⁰.

Results and Discussion

Stress-strain and WAXS. The stretched specimen exhibited the stress-strain curve shown in Fig. 1. The stress value of the second yield maximum is comparable to that of the first yield. Visual observations of the deformation process detected the onset of necking around the second yield. To correlate the mechanical properties shown in the σ - ϵ curve and the changes of crystalline properties, the crystallinity was analyzed as a function of elongation. The different WAXS spectra that were obtained vary systematically with the level of deformation.

The spectra show the two sharp characteristic peaks (110) and (200) of the orthorhombic structure. In general, as a consequence of the deformation, the intensity of the (110) reflection in the stressed state slightly decreases whereas that of the (200) reflection shows important increases. However, when the tension is released the intensity of (110) peak increases for all elongations, while the intensity for the (200) peak decreases for elongations below the second yield but increases for higher elongations. In the released state the intensity of the (110) reflection at the first yield point almost restores its value in the unstretched specimen, which means that the original properties are almost recoverable. Most noticeable is that the (200) peak increased in intensity with the elongation for both states, respect to the (110) reflection.

These changes in the intensities of the orthorhombic peaks may be explained in terms of the orientation. It was reported for LLDPE samples that there was no discernible orientation until the first yield point was reached. The decrease in orthorhombic (110) intensity was directly correlated with the increase in monoclinic ($\bar{2}01$) intensity. At the first yield point the orthorhombic (200) reflection oriented rapidly towards the equator, its intensity increased up to elongations beyond the second yield point but remained constant when reaching the plateau region of the load-extension curve^{7,11}.

Corresponding to the stressed state, coincident with the second yield of the σ - ε curve, a small extra reflection was registered at $2\theta \approx 24.6^\circ$ in all the specimens, initiating from the elongation at $\varepsilon \approx 51\%$ due to the $(\bar{2}01)$ reflection of the monoclinic phase. This phase is a martensitic transformation from the orthorhombic to the monoclinic phase¹¹⁻¹². This reflection increased in intensity until a certain strain was reached ($\varepsilon \approx 65\%$) and then remained constant or decreased as deformation continued. This behavior agrees with that reported for LLDPE by these authors. This monoclinic peak is not stable, since it only appeared in SS but disappeared after the removal of the stress. The strain at which the martensitic transformation starts to occur depends on the crystallinity, and on the strain rate¹². This monoclinic reflection has little contribution to the total crystallinity as compared to those of the orthorhombic reflections (see below).

Crystallinity. The crystallinity degree was determined from the WAXS spectra in the angular interval 15.0 - 27.5° , which only encompasses the very intense (110) and (200) reflections from the orthorhombic structure. We are interested in to determine the evolution of the crystallinity associated to these orthorhombic reflections as a function of the elongation. The crystalline fraction Φ was calculated as the ratio of integral of the orthorhombic crystalline peaks over the sum of integrals of the crystalline and amorphous peaks. That is, using the relation

$$\Phi = \frac{A^{110} + A^{200}}{A + A^{110} + A^{200} + A^{\bar{2}01}} \quad (1)$$

Where A and A^{hkl} are the areas of the amorphous and the hkl reflections. The Φ values in the SS and RS states are presented in Fig. 2. They changed considerably at different strain stages and showed a multi-step plot. Comparing the Φ behavior to the σ - ε curve, the plot in this Fig. 2 can be schematically subdivided into three zones of the elongation. We call the first yield zone that with elongations smaller than $\varepsilon \approx 35\%$, the valley zone that between 35 and 55%, and the second yield zone for elongations higher than 55% but smaller than that where strain-softening ends.

The specimen without deformation had $\Phi = 55\%$. In the first yield zone the Φ value for SS increased to 65% at small elongations (below the first yield point). This increment can be explained by the process of strain-induced crystallization because on initial deformation, the crystallites act as hard inclusions, and the strain in the material is carried predominantly within the amorphous fraction. As deformation continued the Φ value decreased to 58% and remained constant in this first zone, within experimental errors. In the valley zone the Φ shows a significant decrement to a value of 48% which may be associated to the fragmentation of the crystalline lamellae which in turn possibly may cause strain-induced decrystallization. In the second yield zone the Φ had an additional significant decrement to 28% followed by an important increment to 40% and then decreased to about 30%. The first decrement may be associated to partial melting of the less perfect crystallites. However, the increment can only be associated to a recrystallization process. Therefore, the recorded increment of the stress at the second yield point is not a surprise since, in general, the mechanical properties and, in particular, the yield stress increases with Φ , confirmed by the curve shown in Fig. 1. The final decrement in the second yield zone is also related to the neck formation observed, where a temperature rise may occur¹; with the increase of temperature the decrement of crystallinity is expected.

These results identify three well-defined zones associated with the first yield, valley, and second yield points which appear at approximately the same elongation intervals observed in the σ - ε curve. Two most noticeable features are seen in the Φ plot: 1) the fact that significant decrement occurs at the very beginning of the second yield zone may be caused by partial

melting of the crystallites, and 2) the significant increment for elongations in the region of the second yield may be associated to a recrystallization process.

A melting-recrystallization process was discussed and postulated as a possible explanation for the double yield phenomenon. In semi-crystalline polymers chain units are present that are still potentially crystallizable. Further crystallization can be induced in such systems by a uniaxial deformation. On the other hand, partial melting involves the fusion of the less perfect crystallites. It was proposed that during deformation the energy for partial melting comes from the concentration of stress on these less perfect crystallites; thus, it is not necessary for a large temperature increase to take place in order for partial melting to occur². With deformation, the melted material will recrystallize. This crystallization process may be further augmented by the crystallization of some of the initial crystallizable, but not already crystalline units. Thus, with the deformation there is the possibility of two yields based on the original and on the newly formed crystalline lamellae⁵.

The Φ behavior for the RS shows a similar tendency but in a minor extent (Fig. 2). We considered important to include the Φ values in the RS because, being free of the influence from the monoclinic phase, they allow to examine the crystallinity variations due to the exclusive contribution of the history imposed by the plastic deformation. In all cases the Φ values for RS are higher than those for SS. Crystallinity values measured using differential scanning calorimetric technique in a necked specimen, 1 h after unloading, of several LLDPE samples have been reported⁷. For some samples this crystallinity was higher than the crystallinity in the undeformed state and was attributed to stress-induced crystallization, but the value for this unique elongation was not established. Since the necking is presented in the second yield zone, and taking into account our results, we think that this higher crystallinity in necked specimens may be due to recrystallization. The precise mechanisms associated with this behavior (RS values higher than SS values) are still not well understood. However, it may be reasonable to expect higher crystallinity values in RS than in SS because of the absence of the constraints imposed by the stress on the molecular chains.

It is important to compare the contribution of the orthorhombic (110) reflection to the total crystallinity; also presented in Fig. 2. A great parallelism is observed in the second yield zone between the behaviors of these data with those of Φ . It was reported that the decrease in this equatorial orthorhombic intensity corresponded to the formation of monoclinic material^{7,11}. However, the intensity of the monoclinic ($\bar{2}01$) peak is very small as compared to the orthorhombic (110) peak. Its highest contribution to the total crystallinity was of $2.62 \pm 0.04\%$ at $\epsilon = 61.7\%$, this value in terms of the scale used in this figure is about two times the size of the symbol. Therefore, the abrupt decrement observed at the start of the second yield zone is mainly due to the effect of melting.

Conclusions

The WAXS experiments indicated that the double yielding behavior is related to changes of the crystallinity of the stretched specimens at different stages in the course of a tensile test. The uniaxial deformation is a complex, multi-step process, and at various deformation stages some additional mechanisms are activated. The crystallinity as a function of elongation allowed subdividing the double yield phenomenon into three zones: first yield, valley, and second yield. At small strains in the first yield zone strain-induced crystallization was observed. Later, the crystallinity of the orthorhombic phase decreased abruptly in the valley region, associated with

fragmentation of crystalline lamellae. In the second yield zone again decreased and presented an increment followed by an approximately equal decrement. This last behavior is associated with partial melting followed by recrystallization, and the final decrement may be associated to fragmentation of the newly formed lamellae. The crystallinity for specimens in the released state did not have the influence of the monoclinic phase and showed similar behavior as the stressed specimens, although to a relative minor extent.

These experimental results show that the second yield point is not only associated with the deformation of the crystalline portion. They indicate that a process of partial melting of the crystallites followed by a recrystallization takes place in the second yield region. This partial melting-recrystallization process is one of the main mechanisms in the double yield phenomenon.

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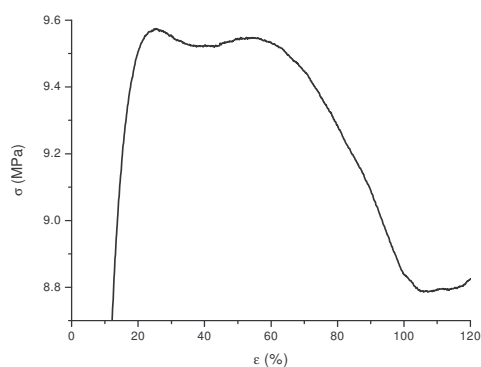


Fig. 1. Stress-strain curve in the double yield region.

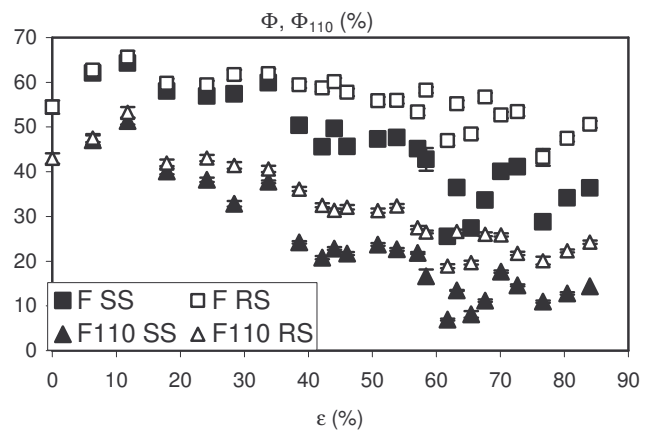


Fig. 2. Total crystallinity and crystallinity associated to the orthorhombic (110) reflection as a function of the elongation.